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# HIGH TEMPERATURE PROPERTIES OF SODIUM

## Fourth Progress Report For Period 1 April to 30 September 1961

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## ABSTRACT

An experimental program has been established at NRL to measure thermophysical properties of sodium and sodium vapor which will be required in the design of turboelectric systems utilizing sodium as the working fluid to 2500°F. This report covers the status of the measurement program and presents thermoelectric stability data for several noble metal thermocouples at 2500°F.

## PROBLEM STATUS

This is a preliminary report on the problem and covers the period for the fifth and sixth quarters; work is continuing.

## AUTHORIZATION

NRL Problem C05-15  
NASA Order Number NTF-92

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### INTRODUCTION

Turboelectric power systems utilizing a metal vapor as the working fluid are attractive for space missions requiring electric power. These power systems will undoubtedly employ a nuclear energy source and several metals are of interest as working fluids: mercury, rubidium, potassium, sodium, and lithium. This Laboratory is under contract with the National Aeronautics and Space Administration to evaluate thermodynamic and transport properties of sodium to 2500°F.

### EXPERIMENTAL PROGRAM

The program has been recently modified at the request of NASA to include only those properties originally planned for the first phase: vapor pressure, P-V-T properties, vapor and liquid density, specific heat of liquid, and radiochemical studies to determine equilibrium solubilities and condensing-vapor corrosion of container metals (columbium and zirconium) in sodium. The measurements to be made should provide, directly or by calculation, all of the thermodynamic entities required to compile accurate temperature-entropy and enthalpy-entropy diagrams for sodium.

As indicated in the previous report (ref. 1), three high-pressure systems for heating and protecting the measurement apparatuses have been built. These include high-pressure furnaces and systems for auxiliary control, gas purification, and evacuation. Two furnaces will be used in an upright position for P-V-T and density measurements; the third will be used horizontally for radiochemical studies.

The high-pressure furnace design was described in detail in the previous report (ref. 1). Unexpected difficulty has been experienced in obtaining a positive seal between the inner chamber and the furnace proper for both upright furnaces. Seals of various types have been tried unsuccessfully. However, a modified silver chloride seal was recently assembled in the P-V-T furnace and preliminary tests indicated a positive closure. Another silver chloride seal was designed and is being built for the density furnace and should be available for test near the end of September. These furnaces could have been employed without positive inner seals, but only at considerable risk since the Nb-1%Zr alloy degrades rapidly with even trace contamination.

Purified argon for protection of the columbium alloy is supplied by passing welding-grade gas through pressurized trains of molecular sieve and heated titanium-sponge (1500 to 1700°F). An electrolytic oxygen analyzer (ref. 1) was built and is being used to monitor the purified gas for traces of oxygen. Tank argon was found to contain between 1.5±0.5 and 10±0.5 ppm of oxygen. Preliminary analyses of the gas after passage through a purification train gave oxygen contents near 0.8±0.5 ppm. No analyses for nitrogen and water vapor have been made.

All welding operations are being performed in a large inert-gas box which is equipped with a high vacuum system and a titanium-sponge purification train for the filling gas. This box has been used very effectively for welding the columbium alloy apparatuses.

Temperature measurements, particularly for the P-V-T apparatus, must be made with extreme accuracy. A study (not in the NASA program) of the factors which influence the stability of thermocouple readings under various conditions of use has been in progress at this Laboratory for about 1-1/2 years. A part of this program, in which couples are being studied in the temperature range from 1800 to 2500°F, is pertinent to the sodium work. Since many property measurements in this temperature range require thermocouples for use in both oxidizing and inert atmospheres, the study has been restricted to noble metal couples: Pt/Pt10%Rh, Pt1%Rh/Pt13%Rh, Pt6%Rh/Pt30%Rh, and Ir/Ir50%Rh.

When thermocouples were given positive protection from furnace contamination, it was found that the principal contribution to thermoelectric instability up to 2500°F was contamination from impurities in the ceramic protection tubes. Other sources, such as junction effects and preferential volatilization of one metal (or oxide) from alloy legs, which may contribute to instability at higher temperatures, were insignificant at 2500°F.

Except for a few tests with magnesia, stability and contamination tests have been limited to wires sheathed in several grades of alumina. Stability tests were made by firing sheathed couples at 2500°F for 120 and 240 hours and rechecking their calibrations relative to reference standards at 1620°F. The influence of the purity of alumina sheathing can be demonstrated by the results of tests with a Pt/Pt10%Rh thermocouple in an argon atmosphere. After firing this couple (20 mil wires) for 120 hours at 2500°F in various grades of alumina, calibration changes at 1620°F, with constant immersion, were as high as -18°F for poorer grades and as low as -1.8°F for the best grade. For the couple exhibiting a calibration shift of -18°F with constant immersion, a decrease in immersion depth resulted in calibration changes greater than -200°F.

The most promising combinations for use in argon to 2500°F are Ir/Ir50%Rh and Pt6%Rh/Pt30%Rh when insulated with alumina of the highest purity obtainable. Either of these couples with 20 mil elements should be sufficiently accurate for measurement requirements in the sodium program. The Pt6%Rh/Pt30%Rh couple is less subject to embrittlement and breakage, but is more susceptible to contamination and calibration change. However, the Pt6%Rh/Pt30%Rh thermocouple, when sheathed in alumina of the highest purity, exhibited a calibration shift of only -0.9°F after constant immersion for 120 hours at 2500°F. Two other platinum-rhodium combinations, Pt/Pt10%Rh and Pt1%Rh/Pt13%Rh, in identical experiments exhibited larger shifts of approximately -2.2°F.

All the noble metal couples were reasonably stable in air at 2500°F; Pt6%Rh/Pt30%Rh exhibited maximum stability and Pt/Pt10%Rh minimum stability. The Pt/Pt10%Rh couple when protected by various grades of alumina and heated for 240 hours at 2500°F exhibited no detectable calibration change in the alumina of highest purity, but changed as much as -2.5°F in lower grades.

## INDIVIDUAL PROPERTY TESTS

### Pressure-Volume-Temperature

A null point method will be used to provide dimerization data, enthalpies, entropies, and specific volumes for vapor states of sodium in the superheat region. Two types of apparatuses are to be used and are shown schematically in Figures 1A and 1B. Both are closed chambers machined from columbium alloy and equipped with flexible diaphragms. The movement of the diaphragm permits the balancing of internal and external pressures so that a measurement of pressure may be made externally with calibrated Bourdon gages.

The apparatus in Figure 1A was designed for visual observation of diaphragm movement and will be used for initial tests of diaphragm operation up to 2200°F using a quartz test tube in the pressure furnace. The position of the diaphragm will be determined by observing the movement of the central sighting post relative to the two stationary outer posts. The central post is machined with a flat disc or follower which is positioned on and free to move with the diaphragm. It is hoped that this follower will reduce diaphragm fluctuations and enhance the reproducibility of its movement.

The more elaborate apparatus shown in Figure 1B is designed for electrical pick-up of diaphragm movement, and will be used in a mullite tube for all P-V-T studies with sodium. When the external pressure is greater than the vapor pressure of sodium inside the chamber, the diaphragm will be flattened against the supporting surface below the probe; and when the pressure differential is reversed, the diaphragm will make contact with the probe and complete an electrical indicating circuit.

Both types of apparatus were designed with thick chamber walls and with thick metal plates on both sides of the diaphragm in an effort to maintain isothermal conditions. Thermocouples are to be installed in wells located at the diaphragm and at the base of the container.

The procedure for charging a null apparatus with sodium will depend to some extent on the life of a given apparatus. If the same apparatus can be used at least twice, distilled sodium will probably be introduced in small solid drops from a tarred container into the apparatus at the filling port. All filling operations, including the weighing of the sodium, will be performed in the large, vacuum-inert gas box. After sodium is introduced into the apparatus, the closure tube permits a thorough degassing and evacuation of the chamber before the tube is closed by welding. Other operational procedures and methods for the analysis of data can be considered more appropriately after experimental data have been obtained. Tests required to determine and correct for surface adsorption, diffusion of gases into the chamber, and other sources of error, will be made as dictated by the experimental results.

Apparatuses of both types have been machined and are being welded. If the new silver chloride seal for the inner chamber of the pressure furnace provides a reliable and positive closure, initial tests of diaphragm operation should be started around the 15th of October.

### Density

Density of sodium to 2500°F will be determined point-wise with small pycnometers (Figure 2) of columbium alloy. The density data will be obtained directly by weighing the sodium remaining in the calibrated volume after equilibration at a given temperature and indirectly by chemical analysis for total alkali of the metal removed from the chamber. The apparatus can be charged by distilling sodium directly into the pycnometer through the filling tube. Final assembly of the top chamber to the pycnometer, degassing, evacuation, and closure are accomplished in the vacuum-inert gas box.

Two density apparatuses have been prepared; if the modified silver chloride seal provides a positive closure in the density furnace, these measurements should start about October 27.

### Specific Heat

Heat contents and specific heats of sodium to 2500°F will be measured with a drop method and a copper-block calorimeter previously described in detail (ref. 2). A specific heat container was machined from Cb1%Zr, filled with sodium, and heated to 2500°F in a vacuum-bell-jar system for two hours with no apparent difficulty. However, an empty columbium alloy container, when heated to the same temperature in the specific heat furnace, exhibited reaction and embrittlement. The calorimeter with present design does not permit the positive protection which is required for the columbium alloy.

A decision was made to use Inconel for containment up to 2200°F, since this alloy was immediately available. An Inconel bucket was filled with sodium and heated to 2200°F for several hours in a vacuum-bell-jar with no apparent difficulty. Heat content determinations are now being made on Inconel containers, with and without standard sapphire, to calibrate the calorimeter and to see if Inconel has the required resistance to thermal shock.

### Equilibrium Liquid Solubilities

The system designed for the study of Cb1%Zr alloy solubility in liquid sodium to 2500°F has been completely integrated and satisfactorily tested. Figure 3 shows a sectional view of the equilibration vessel, which, with the exception of the graphite sampler, is fabricated of the columbium alloy. This partitioned, cylindrical vessel is approximately 2 inches in outside diameter and 3-1/4 inches in length with 1/8 inch walls and reinforced ends. Sodium was vacuum distilled and filtered directly into the equilibration vessel. The vessel was shrouded with zirconium foil, transferred to the controlled atmosphere furnace described in (ref. 1), and isothermally heated to the desired temperature. Upon equilibration of the sodium, the melt was sampled into the graphite crucible by 180° rotation of the apparatus.

One experiment was made in which the columbium alloy was exposed to vacuum distilled sodium at 2389°F for a two-hour period. The test was only partially successful as it was subsequently discovered

that containment of the sodium by the solubility apparatus was incomplete. Approximately 7 grams of the original sodium charge (20 grams) remained for sampling and was successfully contained in the graphite receptacle. This sample has been chemically processed preparatory to analysis by the proposed thermal neutron activation method (ref. 3); however, the sample has not yet been irradiated and no analytical results are reported. The exact reason for the unsuccessful containment of sodium has not been determined, although diffusion through a crystallized weld is possible. This first experiment, while only partially successful from the standpoint of the original objective, was significant in that no radical design changes appear necessary in either the equilibration vessel or the auxiliary systems.

#### Condensing-Vapor Corrosion

This phase of the radiochemical work will follow the liquid solubility study since the same furnace and auxiliary control systems are to be used, and detailed design of apparatus has not been finalized. The measurement will involve radiochemical analysis of sodium condensing off a columbium alloy cold finger into a lined alloy boiler. Preliminary observations from the liquid phase solubility study indicate the potential use of graphite as a suitable material for the liner.



#### REFERENCES

1. C. T. Ewing, J. P. Stone, J. R. Spann, T. A. Kovacina, and R. R. Miller, NRL Memo Report 1165, 10 May 1961
2. B. E. Walker and C. T. Ewing, WADC Technical Report 54-185, Part I, July 1954
3. T. A. Kovacina, "Sodium Liquid- and Vapor-Phase Corrosion Studies at High Temperatures using Radiochemical Methods," presented at NASA-AEC Liquid-Metals Corrosion Meeting, NASA TN D-769, Washington, D. C., December 28, 1960.

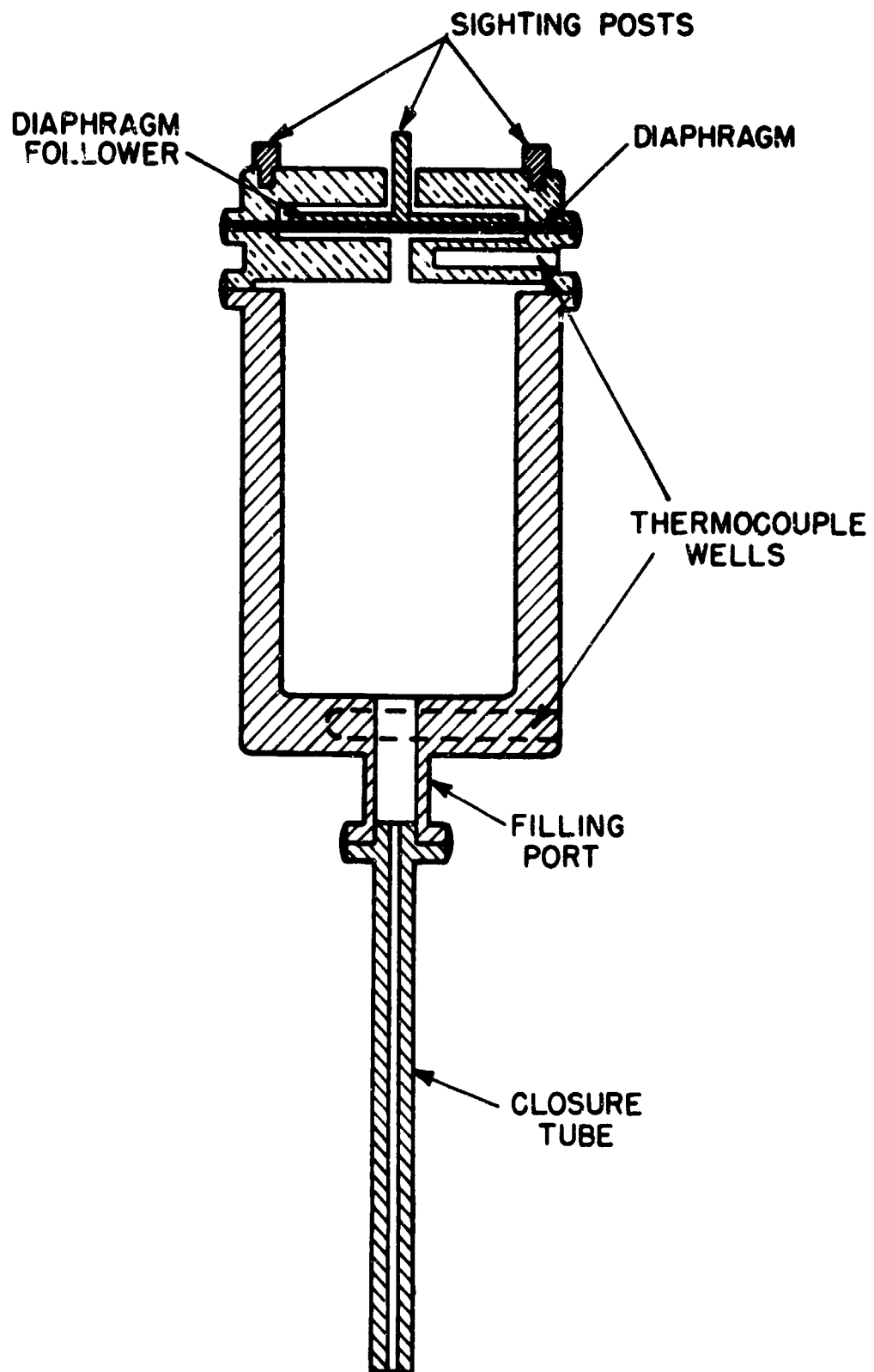


Figure 1a - Null-point Apparatus

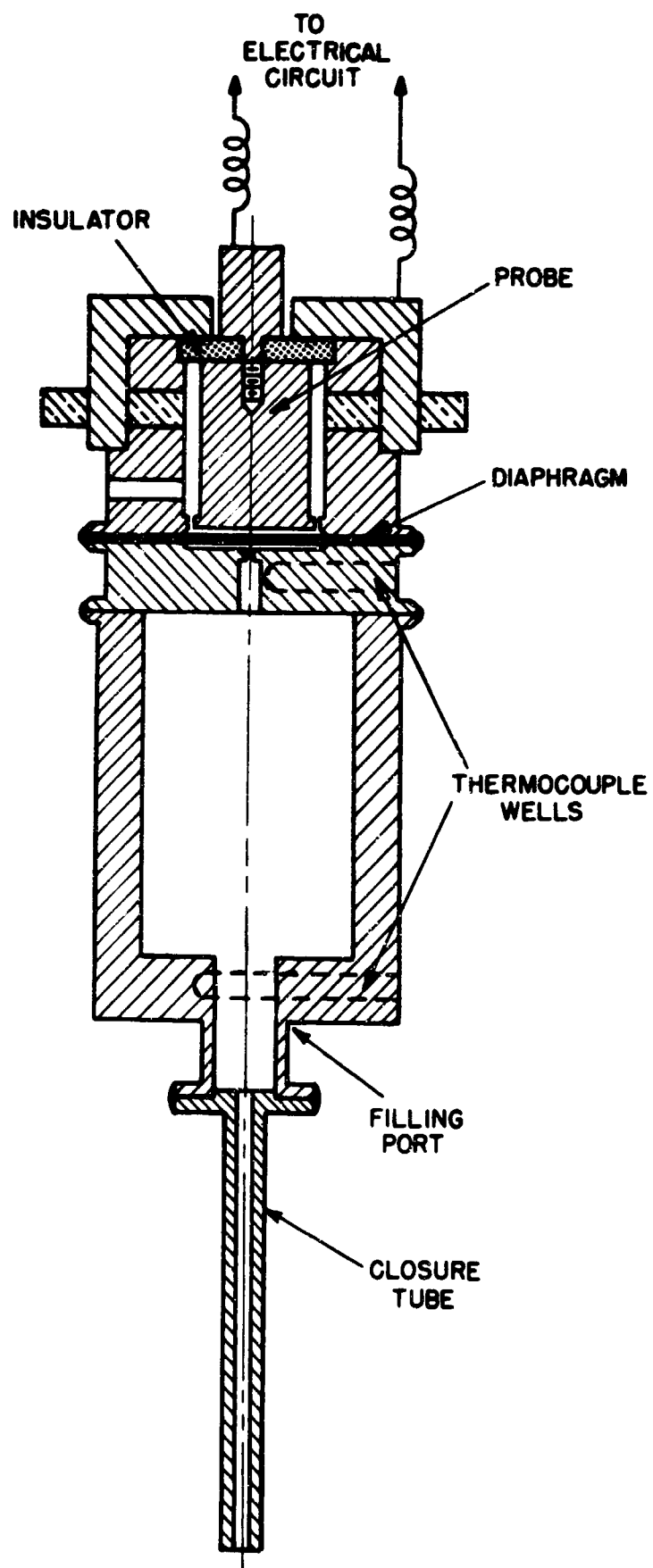


Figure 1b - Null-point Apparatus

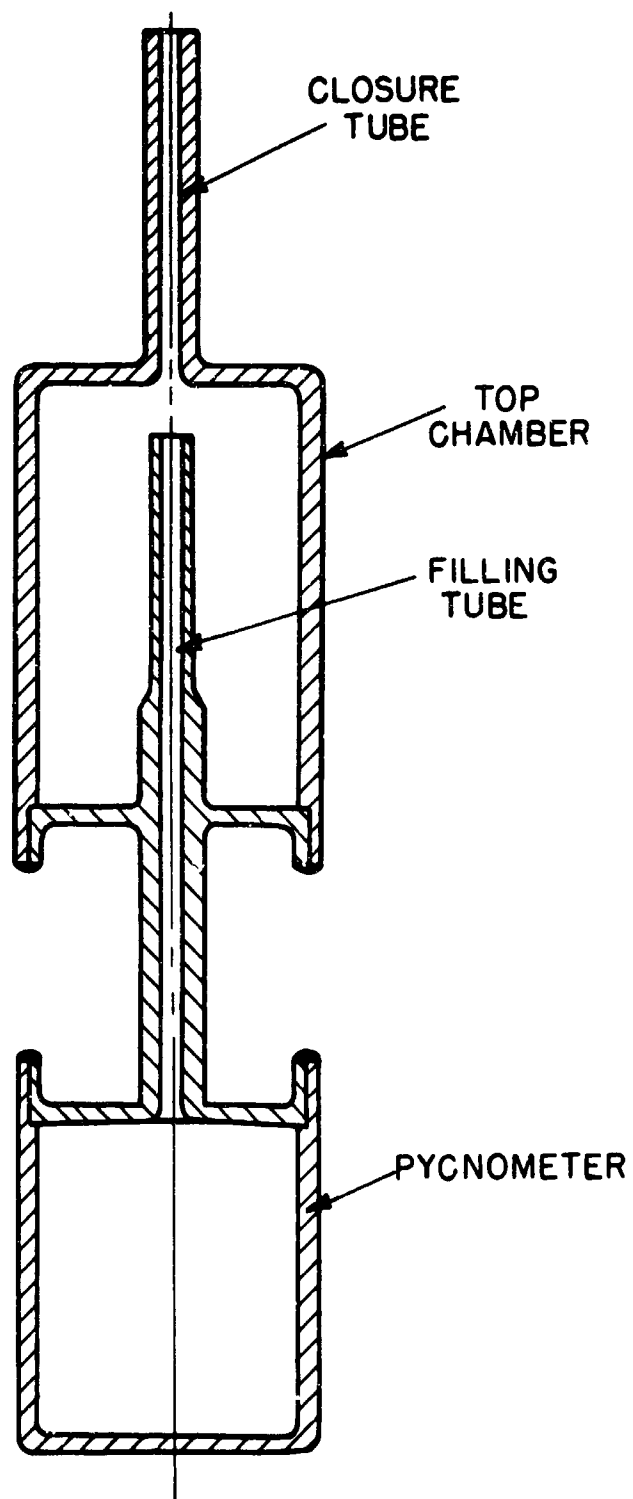


Figure 2 - Density Apparatus

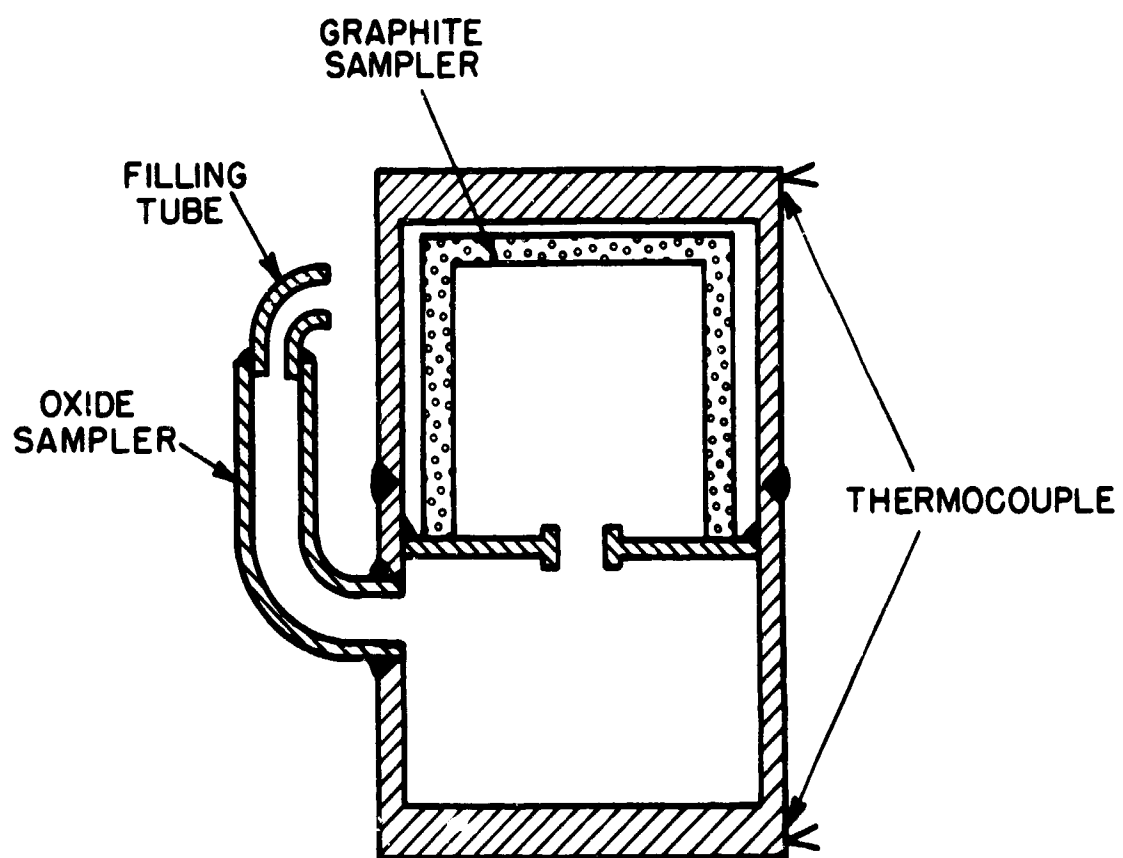


Figure 3 - Liquid Solubility Apparatus